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Temporal trends in the bulk deposition and atmospheric concentration of acidifying compounds and trace elements in the Finnish Integrated Monitoring catchment Valkea-Kotinen during 1988–2011

Tuija Ruoho-Airola[1)], Tarja Hatakka[2)], Katriina Kyllönen[1)], Ulla Makkonen[1)] and Petri Porvari[3)]

[1)] *Finnish Meteorological Institute, P.O. Box 503, FI-00101 Helsinki, Finland*
[2)] *Geological Survey of Finland, P.O. Box 96, FI-02151 Espoo, Finland*
[3)] *Finnish Environment Institute, P.O. Box 140, FI-00251 Helsinki, Finland*

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The precipitation chemistry of nearly 30 acidifying compounds, base cations and several trace elements was monitored in the Valkea-Kotinen catchment in southern Finland during 1988–2011. Measurements of the atmospheric concentration of SO_2, NO_2 and O_3 covered a shorter period. Temporal trends in the components are presented. A notable finding was an indication of a possible increase in the bulk deposition of Cd and NO_3^-. The effect of the changing nitrate deposition on the hydrological continuum of groundwater is also briefly discussed. The transport of air masses to the Valkea-Kotinen catchment was estimated and binds all the results presented in this issue to the development in the emission patterns in Europe.

Introduction

The Integrated Monitoring (IM) Programme is one of the five International Co-operative Programmes carried out under the Convention on Long-Range Transboundary Air Pollution. The aim of the programme is to investigate the influence of transboundary atmospheric deposition on natural ecosystems (Bergström *et al*. 1995). Extensive monitoring of atmospheric deposition is essential for the successful fulfilment of the IM programme and reflects the development in Finnish and European emission patterns.

Results from the first five (Bergström *et al*. 1995) and ten (Ruoho-Airola *et al*. 1998, Ukonmaanaho *et al*. 1998) years of atmospheric deposition monitoring at the Finnish IM stations have been published earlier. Measurements of the atmospheric load now cover 24 years for acidifying compounds, 8–17 years for gaseous compounds and 9–22 years for trace elements. This homogeneous and continuous set of high quality data has enabled us to update existing knowledge of the level and trends in the time series of atmospheric compounds at Valkea-Kotinen, southern Finland. These results have been further used in IM studies on ecosystem effects. In addition, analysis of the uniquely long time series of trace elements is of general interest in relation to the development of the atmospheric

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load in Finland, as well as in examining the relationships between reported European emission reductions and the air concentrations and depositions in relatively remote parts of northern Europe.

Vuorenmaa *et al*. (2009) assessed the deposition data covering 1993–2006 from 33 ICP IM sites in Europe, and the results of monitoring at the four Swedish Integrated Monitoring sites during 1996–2009 have been published in a special issue of *Ambio*. Sulphate (SO_4^{2-}) deposition decreased, whereas no significant change was found in Sweden for nitrate (NO_3^-), chloride (Cl^-) or the base cations (Löfgren *et al*. 2011). In the European Monitoring and Evaluation Programme (EMEP), concentrations and depositions of major atmospheric contaminants have been monitored in a network presently covering most parts of Europe. Results of the monitoring from 1980–2000 have been assessed by Lövblad *et al*. (2004) and from 1972–2009 by Tørseth *et al*. (2012). A large decline was detected in the concentration and deposition of sulphur compounds throughout Europe, but only a moderate decline in nitrogen compounds (Lövblad *et al*. 2004, Tørseth *et al*. 2012). Input/output budgets for the most important trace elements have been determined for 14 ICP IM sites, including Valkea-Kotinen, showing high retention in catchments (Bringmark *et al*. 2013). In the EMEP data, the downward trend for the deposition of the trace elements lead (Pb), cadmium (Cd) and mercury (Hg) has levelled off in recent years (Tørseth *et al*. 2012).

This paper aims to present the atmospheric bulk depositions of the main ions affecting acidification and also of trace elements, as well as gaseous compounds measured at Valkea-Kotinen, and to provide an overview of the development in the time series. In particular, NO_3^- deposition is discussed. The trends in air concentrations and depositions are discussed in relation to trends in European emission reductions.

Methods

A description of the physico-chemical and ecological status, and characteristics of the Valkea-Kotinen catchment site has been published in the five-year report of the monitoring programme by Bergström *et al*. (1995). Site analysis of the Valkea-Kotinen measuring station relative to air pollution emission sources on the mesoscale (from tens of kilometres to about one hundred kilometres) has been compiled in Ruoho-Airola *et al*. (1998), a paper included in a special issue presenting the Finnish IM results. Here, we present a summary of the methods used in the subprogrammes for precipitation, air and groundwater chemistry, as well as methods for trend calculation and sectoral analysis. A detailed description of the methods for monitoring is presented in the Manual of Integrated Monitoring (ICP IM Programme Centre 1998).

The contents of the different subprogrammes covered in this study and the institutions responsible for the monitoring are listed in Table 1. The precipitation chemistry subprogramme has been carried out continuously at the Valkea-Kotinen catchment since the beginning of the IM programme in 1987. Initially, the measurement programme covered the main anions and cations that have an impact on the atmospheric acidification of ecosystems. Later, deposition measurements of trace elements as well as air chemistry monitoring were gradually added to the programme. Meteorological measurements at meteorological stations near the Valkea-Kotinen catchment cover the whole monitoring period.

Sampling and analysis of the precipitation and air chemistry programmes

Measurements of the main anions and cations in precipitation were started in Valkea-Kotinen in April 1987. The site for the sampling of precipitation as well as sulphur dioxide (SO_2) and nitrogen dioxide (NO_2) was an open area in peatland forest about 75 m in diameter. The angle to the nearest trees was below 30° from the rim of the precipitation collector. The sampling height was 1.5 m above the ground level. Lake Valkea-Kotinen is located about 150 m to the north of the sampling site. The Valkea-Kotinen catchment is a protected area of mainly southern boreal upland forest and peatlands, and no agricultural areas are included in the land use of the catchment (Bergström *et al*. 1995).

NILU-type bulk samplers (polyethylene) with an opening of 200 mm were used for the sampling of precipitation. Because the samplers were always open, part of the dry deposition was included in the samples. The weekly samples were combined after visual checking to give monthly samples. Furthermore, anions and cations were analysed by ion chromatography (EMEP Manual 2001). The fulfilment of the ECE/EMEP Data Quality Objectives (EMEP 2001), i.e. a maximum of 15%–25% uncertainty for the combined sampling and chemical analysis, was tested with the help of three parallel sampling devices in 1988–1995 (Ruoho-Airola and Leinonen 1997).

The sampling of most trace elements in precipitation started in 1990. The trace element samples were collected monthly with similar NILU-type bulk deposition samplers to the samples for main ion analysis. For trace element sampling, the collectors were acid-washed. During the early years of sampling, only one sampler was used. In 1992–2007, two replicate samples were collected, but in 2008, replicate sampling was discontinued again after careful consideration and data investigation. The trace element samples were analysed with graphite furnace atomic absorption spectrometry (GF-AAS) until 1993, and with inductively coupled plasma mass spectrometry (ICP-MS) after 1994. Iron (Fe) and chromium (Cr) continued to be analysed with GF-AAS for one additional year, until 1994. Further details on the analysis method and uncertainties are given in Kyllönen *et al*. (2009).

The sampling of total mercury (Hg_{tot}) in precipitation (bulk deposition) started in 1995 at Uraani, in the Janakkala research area (61°01´N, 24°45´E, 31 km to the southwest from the Valkea-Kotinen IM area). A detailed description of the site is provided in Porvari (2003). In 2005, sampling was relocated to Valkea-Kotinen. For the bulk deposition sampling, two duplicate IVL-type collectors were installed in an opening in the forest. In order to estimate the Hg_{tot} concentrations in precipitation for the winter period (December to March), snow samples from an opening in the forest were taken into Teflon® bottles at the end of March. The precipitation amounts were measured at the nearby meteorological station. Since 2010, a single IVL-type collector has been used around the year and the samples have been collected and analysed according to SFS-EN 15853:2010 and SFS-EN ISO 17852:2008 with minor exceptions.

Table 1. Precipitation, air quality, ground water and meteorological measurements in the Valkea-Kotinen Integrated Monitoring area. Responsible institution abbrevaiations: FMI = Finnish Meteorological Institute, FEI = Finnish Environment Institute, GTK = Geological Survey of Finland.

Subprogramme	Responsible institution	Frequency of sampling	Components measured	Start of sampling	End of sampling
Precipitation chemistry	FMI	1 month	H^+, Cl, NO_3, SO_4, NH_4, Mg, Ca, Na, K	1.IV.1987	
	FMI	1 month	Zn, Pb, Cu, Cd, Cr, Fe, Mn, V	1.VI.1990	
	FMI	1 month	Ni, As	1.I.1990	
	FMI	1 month	Al, Co	1.I.2003	
	FEI	1 month	Hg*	1.VII.1994	XII.2009
	FMI	1 month	Hg	1.IX.2009	
Air chemistry	FMI	1 month	SO_2	1.I.1996	31.XII.2003
	FMI	1 month	NO_2	1.I.1996	31.XII.2007
	FMI	1 hour	O_3	30.XI.1994	
Meteorology	FMI	1–24 hours	precipitation, temperature, humidity, wind velocity and direction, UV radiation	1.IV.1987	
Groundwater chemistry	GTK	3 months	pH, H^+, Cl, NO_3, SO_4, Mg, Ca, Na, K, HCO_3, alkalinity		

* Sampling from 1994–2004 in the Janakkala research area, approximately 30 km from Evo.

Concentrations of SO_2 and NO_2 were measured with IVL-type diffusion samplers (Ferm 1991). Monthly samples were collected using two parallel samplers and field blanks were subtracted from the results. In the sampler, SO_2 was trapped on Whatman 40 filter paper (∅ 25 mm) impregnated with 1% NaOH (in methanol). To collect NO_2, similar Whatman filters were treated with a solution containing 9% NaI and 1% NaOH. After exposure, the sample filters were extracted in HPLC-grade water. The SO_2 filter extracts were filtered and analysed for SO_4^{2-} by ion chromatography (Waters). The NO_2 filter extracts were analysed colorimetrically at 540 nm for nitrite, after mixing with a diazotizing reagent (EMEP 2001). Ozone (O_3) was monitored 4 km to the southeast of Valkea-Kotinen by UV photometry. The calibration of the monitor is traceable to the Finnish reference at the national reference laboratory on air quality (www.fmi.fi).

The Geological Survey of Finland (GTK) has monitored groundwater quality in southern Finland since 1969 (Backman *et al*. 1999). Water quality was investigated from 1974 to 2010 at Kellolähde near the Valkea-Kotinen catchment (61°00´N, 25°12´E, 27 km to south from the Valkea-Kotinen IM area). Before 1995, the groundwater samples were taken six times per year, and after this four times per year. The Kukonharju–Sipilänharju sand and gravel formation is a large groundwater reservoir, and groundwater discharges into the Kellolähde spring, which is in a natural condition (Backman *et al*. 1999, Backman 2004). NO_3^- concentrations in groundwater were analysed at the geochemical laboratory of GTK (later Labtium Oy) from untreated water samples initially by spectrophotometry and from 1989 by ion chromatography (Backman *et al*. 1999).

Trend analysis

A generalized least-squares (GLS) regression with classical decomposition and autoregressive moving average (ARMA) errors used for monthly mean values was carried out using the method of Brockwell and Davies (2002) (ITSM Professional 7.3, B and D Enterprises Inc.). The detailed steps used for the calculation of the seasonal components by a moving average with a 13-month window, a preliminary regression model for the trend in the deseasonalized data, the iteration of the optimal ARMA(p,q) model for the residuals and the final estimates for the trend and error structure are described in Anttila and Tuovinen (2009). Further principles of the method are presented in Brockwell and Davies (2002).

Sectoral analysis

The transport of the air masses to the Valkea-Kotinen area was analysed using two-dimensional 925 hPa backward trajectories of 96 h obtained from the EMEP MSC-W (www.EMEP.int). The air parcel was tracked every 2 h along modelled wind fields, and the trajectories were calculated four times per day. The area around the arrival point was divided into eight equal sectors. The criterion for the allocation of the trajectories of a particular arrival day to a specific sector was that at least 50% of their given positions during transport were found within that sector. If this criterion was not fulfilled, the sector for that day was set as undetermined. Finally, the number of days with transport from the corresponding sector was counted. In analysing the differences in transport between seasons, the months from October to March were included in the winter season, and the months from April to September in the summer season. The detailed steps used for the transport analysis are presented in Ruoho-Airola *et al*. (2004).

Results and discussion

Acidifying compounds in deposition

Annual bulk deposition

The total monitoring period of the main anions and cations covered 24 years. The annual deposition levels of the components were evaluated from 10-year mean values, which filtered away the less interesting short-term variation in the time series. The averaged periods always overlapped by five years: 1988–1997, 1993–2002, 1998–2007 and 2003–2011 (the last period cov-

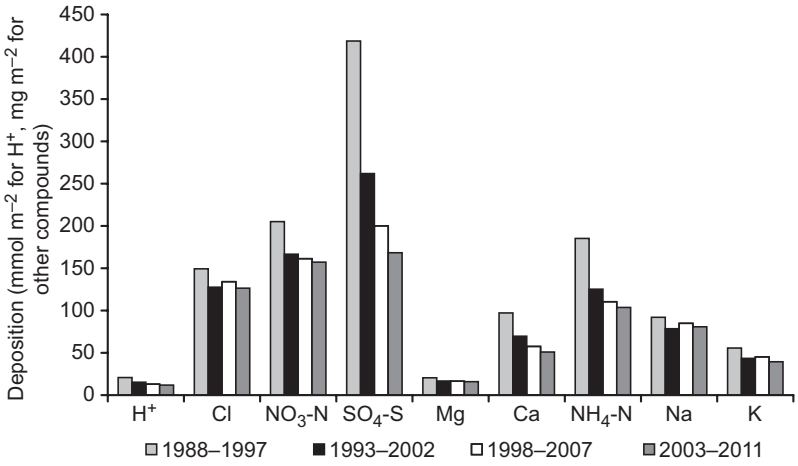

Fig. 1. Ten-year annual mean values for the bulk deposition of the main anions and cations at Valkea-Kotinen.

ered only nine years). This procedure enabled changes in the average level of the annual deposition to be followed in five-year steps.

For all the main anions and cations, the deposition was highest during the first period from 1988 to 1997 (Fig. 1). At that time, the mean deposition values for SO_4^{2-}, calculated as sulphur (S), and NO_3^- and NH_4^+, calculated as nitrogen (N), were 419, 205 and 185 mg m^{-2}, respectively. Depositions of Cl^- and hydrogen ions (H^+) were 149 mg m^{-2} and 21 mmol m^{-2}, respectively. Finally, mean depositions of the base cations sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) at the beginning of the monitoring period were 92, 56, 97 and 21 mg m^{-2}, respectively. The deposition levels at Valkea-Kotinen were comparable to results measured at other background stations in southern Finland (Kulmala *et al*. 1998) and the other Nordic countries (Lövblad *et al*. 2004, Löfgren *et al*. 2011, Tørseth *et al*. 2012).

For SO_4^{2-}, the decline from average deposition in 1988–1997 to that in 1993–2002 was considerable, being 35%, which reflected the large decrease in sulphur emissions in Finland and elsewhere in Europe (Lövblad *et al*. 2004). Similar results have been reported from other monitoring stations in Finland and northern Europe (Lövblad *et al*. 2004, Tørseth *et al*. 2012). In addition, mean ammonium deposition declined almost as much during the same period. The majority of the Finnish atmospheric sulphur load results from long-range ammonium-sulphate transport (Nyíri *et al*. 2010), which explains the parallel decline in these components. NO_3^- deposition also declined by almost 20% during the first half of the monitoring period, partly due to the decrease in nitrogen dioxide emissions in Finland and elsewhere in Europe (Lövblad *et al*. 2004). The long-range transport accounted for about 90% of NO_3^- deposition at Valkea-Kotinen (Nyíri *et al*. 2010). However, the transport and deposition of S, NO_3^- and NH_4^+ are linked through air chemistry (Seinfeld and Pandis 2006), which creates nonlinearities in the changes in deposition as compared with the changes in emissions (Fowler *et al*. 2005). The decrease in SO_2 emissions has led to a shift towards the formation of more ammonium nitrate particles (Fagerli and Aas 2008).

Average depositions of the base cations Na^+, K^+, Ca^{2+} and Mg^{2+} declined by 15%–30% between the periods 1988–1997 and 1993–2002. This result is consistent with the decline of 15%–35% in total depositions of the base cations recorded for the whole of Finland between the years 1989 and 2000 (Ruoho-Airola *et al*. 2003) and in other European countries (Tørseth *et al*. 2012). The change is considered to have mostly originated from the decline in anthropogenic emissions. The mean deposition of H^+, which reflects the changes in all of the acidifying compounds, declined by 25% between the two first 10-year periods.

Later, the deposition levels did not change as strongly as at the beginning. During the final

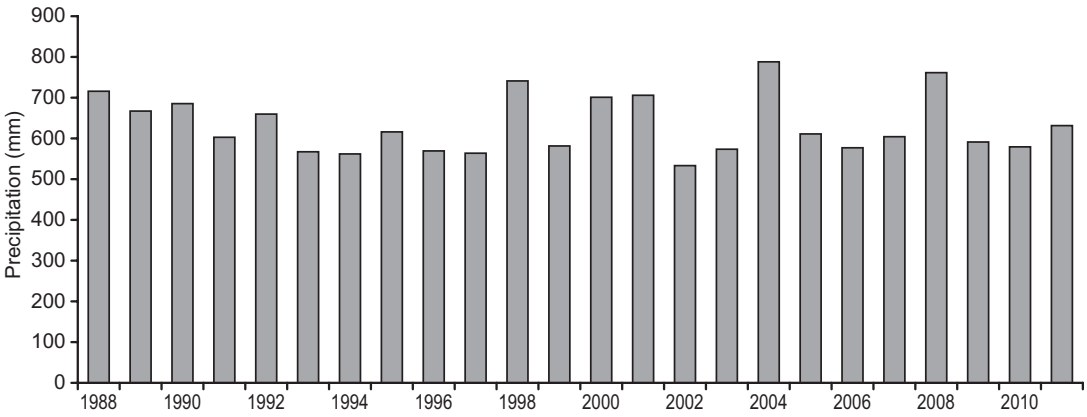

Fig. 2. Annual precipitation at the Lammi Biological Station, near the Valkea-Kotinen monitoring station.

years of the monitoring period, the mean deposition level was 40% of the level at the beginning for SO_4^{2-}, 50%–60% for H^+, NH_4^+ and Ca^{2+} and 70%–80% for K^+ and NO_3^-. Deposition of the compounds largely derived from sea spray, i.e. Cl^-, Na^+ and Mg^{2+}, at the end was 80%–90% of the level at the beginning.

Precipitation at the Lammi Biological Station shows rather large inter-annual variation (Fig. 2). This is the nearest station (*see* fig. 1 and table 1 in Jylhä *et al*. 2014) with a continuous time series of precipitation. The highest annual precipitation was 788 mm in 2004, whereas the minimum precipitation was 533 mm in 2002. The level of precipitation strongly affects the calculation of deposition, which is formed by multiplying the concentration of the component in a rainwater sample by the amount of precipitation collected by the sampler. However, a large amount of rain does not necessarily mean a high level of deposition. For example, SO_4^{2-} deposition in Valkea-Kotinen was 167 mg S m^{-2} in both 2002 and 2004, showing no direct influence of the minimum or maximum rainfall amount.

Trends in the deposition of acidifying compounds within 10-year periods

The previous chapter presented the average deposition levels and changes in the levels between 10-year periods. In order to analyse the pattern of the time series in detail, statistical trend analysis within each of the 10-year periods was performed. Because the ITSM time series analysis used for the calculations can handle the seasonality in the data, the calculations were applied to monthly deposition. The greater number of data points per year also enabled the analysis of shorter time series for NO_3^- deposition (*see* the next chapter).

The ITSM analysis was performed for all main ions and all periods, i.e. 1988–1997, 1993–2002, 1998–2007 and 2003–2011. For the deseasonalized time series, the GLS linear regression and the optimal ARMA structure for the residuals was calculated.

A statistically significant decreasing trend was found for all of the main anions and cations in the period 1988–1997 (Table 2). SO_4^{2-} and NH_4^+ declined equally by 7.5% per year during this decade, and Ca^{2+} by almost as much (7%). All the other compounds declined annually by 4%–6%. The annual change in the amount of precipitation was 2%, which might have partly affected the deposition pattern of the chemical components.

In the other periods, only a few significant trends were detected in the time series of the components (Table 2). SO_4^{2-} declined in all 10-year periods, but the value of the slope decreased with time. H^+ deposition likewise decreased through the whole time series, reflecting the strongly acidifying effect of sulphate deposition. In addition to these changes, NH_4^+ and Ca^{2+} deposition declined during 1998–2007 and Mg^{2+} during 2003–2011.

Trends in the deposition of SO_4^{2-}, NO_3^-, H^+ and (Ca^{2+} + Mg^{2+}) at 33 IM sites in Europe was calculated for 1995–2006 by Vuorenmaa *et al*. (2009). In Sweden, Norway and the Baltic countries, the development in the deposition was fairly similar to the pattern at Valkea-Kotinen: SO_4^{2-} and H^+ widely decreased, whereas for depositions of NO_3^- and base cations only a few significant downward trends were detected.

Detailed analysis of nitrate deposition and nitrate changes in ground water

Nitrate deposition was further analysed with the ITSM programme because of the possible increase in deposition. Between 1988 and 1990, NO_3^- deposition declined steeply, the annual change being –17% (Table 3). During the next years, from 1991 to 1997, the annual change was clearly lower, –6%. After a short period with no significant change, deposition turned to an increase of 5.5% per year, lasting for the period from 2002 to 2008. Despite the rather wide confidence limits for the annual increase in nitrate deposition during 2002–2008 (Table 3), the change is statistically significant and should be understood as an early warning of increasing nitrate deposition. The three most important contributors to the deposition of oxidized nitrogen in Finland are, according to the EMEP estimates, Russia, Finland and shipping emissions from the Baltic Sea and the North Sea, all with an approximately 20% share (Gauss *et al*. 2012). Between 2000 and 2009, two of these increased (Tørseth *et al*. 2012). The nitrogen oxides (NO_x) emissions from Russia increased by 35%, the same change also being estimated for the emissions from the St. Petersburg area, and the emissions from shipping grew by 15%–20% (Tørseth *et al*. 2012). According to a more detailed analysis of the Baltic Sea shipping emissions based on the messages of the automatic identification system (AIS), which enable the positioning of ships with a high spatial resolution (Jalkanen *et al*. 2013), the NO_x emissions were 17% higher than the EMEP estimates (Bartnicki *et al*. 2010, 2011) and increased by 14% between 2006 and 2008 alone. An even larger increase in emissions from ships was detected in the Gulf of Finland,

Table 2. Results of the trend analysis based on the GLS-ARMA method for the main ions. Only statistically significant trends ($p < 0.05$) in the time series are shown. The slopes with the standard errors (SE) are given in mg m^{-2} $month^{-1}$ (for H^+ mmol m^{-2} $month^{-1}$). Annual changes (%) with their 95% confidence limits (CL) are also given.

Component	1988–1997		1993–2002		1998–2007		2003–2011		1988–1997		1993–2002		1998–2007		2003–2011	
	slope	SE	slope	SE	slope	SE	slope	SE	change per yr. (%)	95% CL	change per yr. (%)	95% CL	change per yr. (%)	95% CL	change per yr. (%)	95% CL
SO_4-S	–0.36	0.07	–0.14	0.03	–0.07	0.01	–0.05	0.02	–7.6	2.9	–5.4	2.2	–4.3	0.9	–3.6	3.0
NO_3-N	–0.11	0.02							–5.7	2.4						
Cl	–0.07	0.02							–4.9	2.4						
NH_4-N	–0.16	0.03			–0.03	0.01			–7.5	3.2			–3.7	2.8		
H^+	–10.5	1.1	–7.0	1.6	–2.2	0.5	–3.6	1.6	–5.3	1.1	–4.9	2.3	–2.2	0.9	–3.6	3.3
Na	–0.04	0.01							–4.3	2.6						
K	–0.03	0.01							–5.6	4.2						
Ca	–0.08	0.01			–0.02	0.01			–7.2	2.6			–3.5	2.8		
Mg	–0.009	0.002					–0.002	0.001	–4.8	2.5					–1.8	1.3
Precipitation	–0.11	0.03							–2.3	1.3						

100 km from Valkea-Kotinen in the direction of frequent transport of air masses to Valkea-Kotinen (*see* section 'Transport of air masses to Valkea-Kotinen'). However, the domestic NO_x emissions declined by 25% and the total European emissions decreased by 7% between 2000 and 2009 (Tørseth *et al*. 2012). We assume that our method can detect an early indication of the increase in NO_3^- deposition, even if it was only detected during the years 2002–2008. In an analysis of the EMEP monitoring data covering the 2000s, the average reduction in oxidized nitrogen was 12% in precipitation and 1% on particles, while some stations even measured an increase (Tørseth *et al*. 2012).

For the recovery processes of the environment, the finding of a recent increase in the NO_3^- deposition is a serious signal. As N retention is high in the terrestrial ecosystem of Valkea-Kotinen (Vuorenmaa *et al*. 2012), the increased deposition might raise the risk of saturation and excess leaching of NO_3^- to surface waters. N has played a minor role in acidification in the past, but its relative importance is increasing because the N emissions have decreased much less than the S emissions. The increase in NO_3^- deposition might also strengthen the eutrophication of the Valkea-Kotinen ecosystem.

The concentrations of elements in the groundwater reflect the surrounding soil type and bedrock, as well as atmospheric deposition. The time series of the NO_3^- concentration in groundwater from the Kellolähde spring enabled a preliminary study of whether the unusual pattern of NO_3^- bulk deposition could be detected in groundwater. The trends in the NO_3^- concentration in Kellolähde groundwater were also calculated with the ITSM program and showed a significant increase between 1987 and 1993, and a decrease between 1994 and 2000. The turning point in the concentration was about five years later than that for the bulk deposition. Both groundwater concentrations and depositions were smoothed with a filter, where the weighting coefficients are set to correspond to the ordinates of a Gaussian probability curve in order to remove the short-term variation and reveal the longest wavelength in the time series (Fig. 3). This smoothing method has been recommended (Mitchell *et al*. 1966) and used for meteorological time series analysis (Lindström and Alexandersson 2004). The Pearson correlation between the smoothed time series was high ($r_p = 0.96$, $p < 0.01$, $n = 81$), suggesting an influence of NO_3^- deposition on the general behaviour of the concentration in groundwater after a time lag of five years. Even for the original time series with dense short-term variations, a moderate correlation ($r_p = 0.46$, $p < 0.01$, $n = 81$) was detected. However, the NO_3^- concentration in groundwater levelled off after 2007, and did not show an increase, as occurred for bulk deposition after 2002. According to Backman (2004), the time lag between precipitation and groundwater quality, based on pH values in Kellolähde spring, was about two years. Our preliminary comparison suggested a longer time lag for NO_3^-. This longer period is supported by the results of Kubin (1998) in a case involving the clear felling of two forests, where the nitrate concentrations in groundwater started to rise in the 3rd to 5th summer following site preparation. The groundwater wells were from 4 to 5 m in depth, and the depth of the groundwater varied seasonally, the mean being about 3 m (Kubin 1998). In the Kellolähde area, the minimum thickness of Quaternary deposits is 30 m (Backman 1999), so it could be assumed that the retention time for nitrate transport there could be longer, and even up to five years.

Table 3. Detailed analysis of nitrate bulk deposition at Valkea-Kotinen. Only statistically significant trends ($p < 0.05$) in the time series based on the GLS-ARMA method are shown. The slopes with standard errors are given in mg m^{-2} $month^{-1}$. Annual changes (%) with their ±95% confidence limits (CL) are also given.

	1988–1990	1991–1997	1998–2001	2002–2008	2009–2011
Slope ± SE	–0.39 ± 0.08	–0.10 ± 0.03	–	0.05 ± 0.02	–
Annual change ± 95% CL	–16.6 ± 6.6	–6.4 ± 3.7	–	5.5 ± 4.5	–

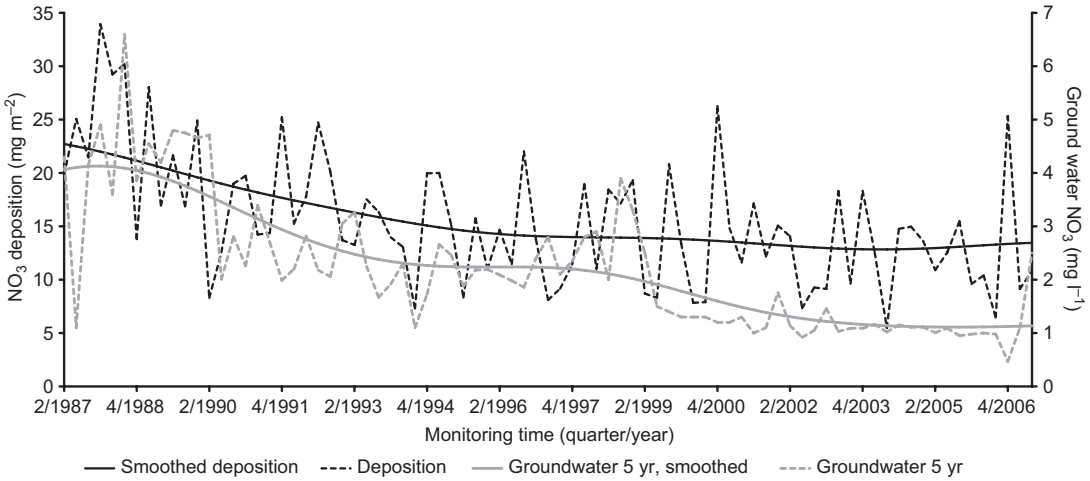

Fig. 3. Nitrate bulk deposition and nitrate in groundwater at Valkea-Kotinen. Groundwater concentrations are moved backwards by five years along the time axis to make the maximum periods overlap. Solid lines present original data smoothed with a filter with weights from the Gaussian distribution.

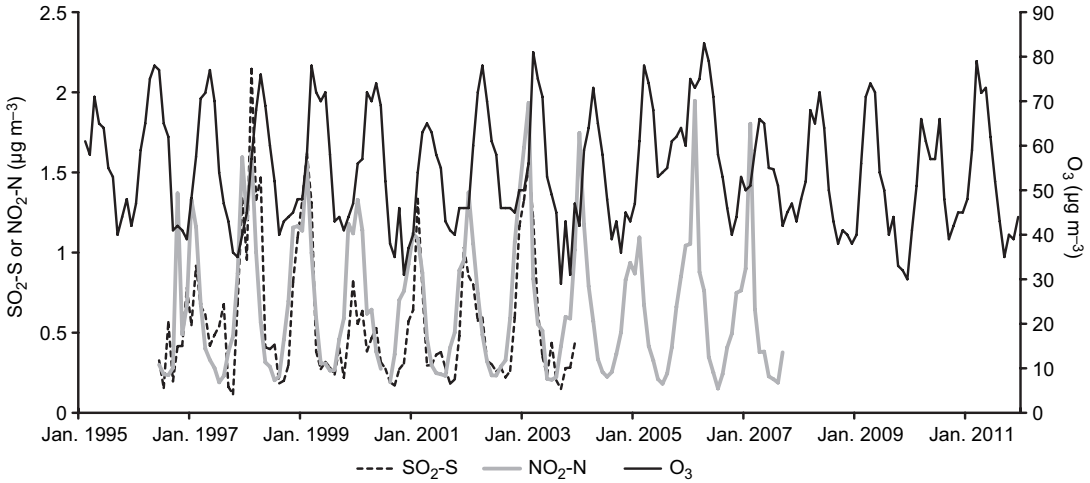

Fig. 4. Time series of the gaseous compounds at Valkea-Kotinen.

Gases

The time series of SO_2, NO_2 and O_3 were shorter than those for depositions of the main ions, being 8, 10 and 17 years, respectively. The high seasonal variation is typical for gaseous compounds (Fig. 4). Levels measured at Valkea-Kotinen were consistent with results from other background stations in southern Finland (Kulmala *et al*. 1998, Anttila and Tuovinen 2009). For SO_2 and NO_2, no statistically significant changes in the time series were detected. Instead, the mean monthly increase (± SE) in O_3 during 1998–2007 was 0.05 ± 0.02 μg m^{-3}. The annual change (± 95% CL) was 1.1% ± 0.8%.

The measurement period for the gases, especially for the acidifying compounds, was too short to provide full support for the effect studies in IM. Data from other southern Finland background stations, such as Ähtäri (ca. 160 km from Valkea-Kotinen), could be used to complete the pattern. The atmospheric concentrations, seasonal behaviour and trends of the S compounds and NO_3^- are mainly controlled by changes in the well-mixed air masses over southern Finland, and were thus similarly recorded at two back-

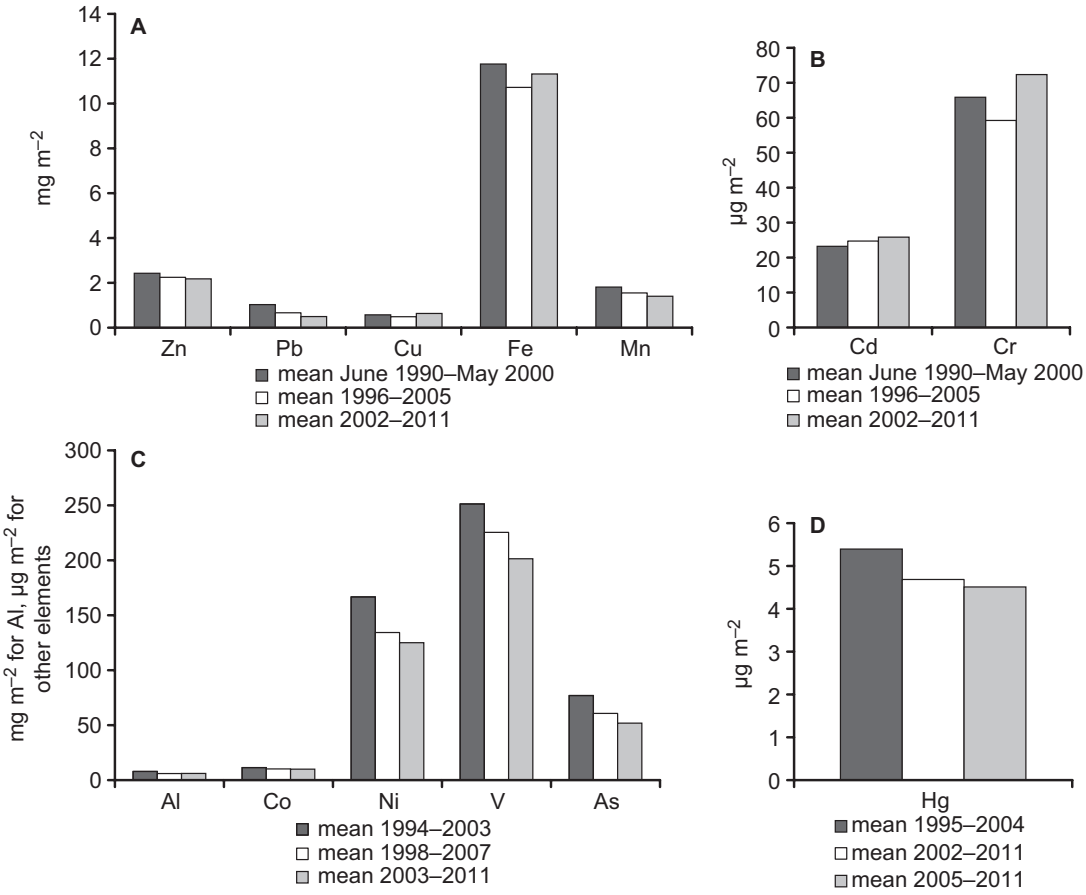

Fig. 5. Ten-year mean values of the bulk deposition of trace elements at Valkea-Kotinen. Note the different units for the separate components in **C**. For Al and Co (in panel **C**), the first column is the annual sum for 2003 and the second is the mean annual deposition for 2003–2007.

ground stations 70 km apart in a comparison of seven years of data (Ruoho-Airola 2012).

Trace elements

Annual bulk deposition

Since the starting time of monitoring of selected elements varied, three approximately 10-year periods were chosen to illustrate the levels of bulk deposition of the elements during their entire monitoring (Fig. 5). For zinc (Zn), Pb, Cd, copper (Cu), iron (Fe), manganese (Mn) and chromium (Cr), these periods were 1990–2000, 1996–2005 and 2002–2011, while for nickel (Ni), vanadium (V) and arsenic (As), the periods covered the years 1994–2003, 1998–2007 and 2003–2011. Finally, for Hg_{tot}, the periods covered the years 1995–2004, 2002–2011 and 2005–2011, where the first period included data only from the Janakkala station, the second period data from both Janakkala and Valkea-Kotinen, and the third period comprised only Valkea-Kotinen data.

The average bulk deposition of Pb decreased by 35% between each of the three 10-year periods, while for As the decline was about 20% (Fig. 5). Lower reductions in the mean annual levels were measured for Zn, Mn, Ni and V. For Hg_{tot}, the mean levels in 2002–2011 and 2005–2011 were about 15% lower than that in 1995–2004. However, translocation of the measurement site from Janakkala to Valkea-Kotinen in 2005 may have had some influence on Hg_{tot} concentrations, even though the sites were

located only 30 km apart. In contrast to the other elements, the Cd level increased by 5% between the periods (Fig. 5).

The measured levels of trace elements were somewhat higher than at most other Finnish background stations, but close to or lower than the levels at background stations in Sweden, Norway and Germany (Bringmark *et al*. 2013, Kyllönen *et al*. 2009). Domestic emissions are higher in the southern part of Finland, where the influence of the heavy European emission sources is also stronger than elsewhere in the country.

A recent paper by Kyllönen *et al*. (2009) discusses the trace element levels in detail and also includes data from the Valkea-Kotinen station.

Trends in bulk deposition of trace elements

The ITSM analysis of trace elements was performed for the same 10-year periods as for the annual bulk depositions. The outcome of the trend analysis can be summarized as follows: (1) during the first 10-year period, the bulk deposition of all elements except Cd and Hg_{tot} decreased; (2) Cd, Fe and Cr deposition increased during 1996–2005; (3) the decline in Pb, As, Ni and V deposition covered the whole measurement period (*see* Table 4).

The trace elements can be grouped according to their enrichment factors, which compare the amount of the element to a reference element assumed to be entirely from crustal sources. Cd, As, Pb and Zn are highly enriched and mostly of anthropogenic origin. Cu, Ni and V are less enriched, but still significantly so. Mn, Cr, Co, Al and Fe are only slightly enriched and generally of crustal origin, with crustal weathering and wind re-suspension being important sources. (Berg *et al*. 1994, Kyllönen *et al*. 2009). For the IM programme, the components having higher enrichment factors are the most interesting ones and are discussed in detail here.

Anthropogenic trace element emissions decreased in the 1980s and 1990s due to strict emission regulations and consequent improvements in the control technologies in Finland and elsewhere in Europe (Pacyna and Pacyna 2001). The reduced emissions, together with the slight decrease in the precipitation amount, have led to a decline in the bulk deposition of trace elements of anthropogenic origin, except for Cd, which increased at Valkea-Kotinen by 2% annually between 1996 and 2005. Cd deposition also increased between 1996 and 2005 at three of the six other Finnish background stations of FMI (data not shown). The annual change was 3% ± 2% in Oulanka, 6% ± 5% in Hailuoto and 11% ± 7% in Pallas. In the EMEP data, the decline in Cd deposition also levelled off at several sites after 2000 (Tørseth *et al*. 2012). In addition, the deposition of Cd increased in Russia between 2000 and 2005 (Travnikov *et al*. 2012). For the Finnish Cd deposition, foreign sources contributed 50% and 70% in 1990 and 2000, respectively (Travnikov *et al*. 2012), and domestic factors therefore also affected the Cd level. The wind re-suspension of cadmium accumulated in soil significantly contributes to cadmium deposition (Travnikov *et al*. 2012), and its amount might vary considerably depending on changing meteorological factors, including the length of the snow-free period (Kyllönen *et al*. 2009). In an earlier study based on annual bulk deposition values and covering all Finnish background stations, no significant change in Cd deposition was detected between 1998 and 2007 (Kyllönen *et al*. 2009), which shows the higher power for detecting trends with the ITSM method using monthly values. Evidently, the pattern of the highly harmful Cd deposition has changed in background areas of Finland, and further research on this is needed.

Pb and As deposition in Valkea-Kotinen declined during all periods calculated. Pb emissions and depositions have decreased widely in Europe due to the introduction of low-leaded and unleaded gasoline (Pacyna and Pacyna 2001, Travnikov *et al*. 2012). Emissions of As have strongly declined in Poland, which has most likely had a considerable effect on the Finnish deposition (Travnikov *et al*. 2012).

Ni and V depositions decreased in 1994–2003 and 2003–2011. These elements are intermediately enriched, oil combustion being an important emission source for both (Pacyna and Pacyna 2001). Domestic emissions of Ni have decreased since 1990 (www.ymparisto.fi/fi-FI/Kartat_ja_tilastot/Ilman_epapuhtauksien_paastot), but for V the domestic emission time series

Table 4. Results of trend analysis based on the GLS-ARMA method for the bulk deposition of trace elements. Only statistically significant trends ($p < 0.05$) in the time series are shown. For Al, Co and Hg no significant trends were detected for any of the periods. The slope is given in μg m^{-2} month^{-1} with a standard error (SE). Annual changes (%) with their 95% confidence limits (CL) are also given.

	VI.1990–V.2000		1996–2005		2002–2011		VI.1990–V.2000		1996–2005		2002–2011	
	slope	SE	slope	SE	slope	SE	change per yr. (%)	95% CL	change per yr. (%)	95% CL	change per yr. (%)	95% CL
Zn	–0.61	0.28					–3.1	2.8				
Pb	–0.69	0.13	–0.19	0.07	–0.19	0.08	–6.5	2.3	-3.4	2.3	–4.4	3.4
Cd			0.003	0.001					2.0	1.6		
Cu	–0.20	0.01					–3.9	0.5				
Fe	–5.18	1.36	3.60	1.28			–4.8	2.5	6.4	4.4		
Mn	–0.57	0.24					–3.7	3.0				
Cr	–0.03	0.01	0.03	0.01			–5.2	3.5	10.4	7.6		
	1994–2003		1998–2007		2003–2011		1994–2003		1998–2007		2003–2011	
	slope	SE	slope	SE	slope	SE	change per yr. (%)	95% CL	change per yr. (%)	95% CL	change per yr. (%)	95% CL
Ni	–0.07	0.03			–0.07	0.02	–4.5	4.1			–6.2	3.5
V	–0.10	0.02			–0.11	0.03	–4.5	1.9			–5.6	3.0
As	–0.05	0.01	–0.03	0.01	–0.02	0.01	–6.1	2.2	–4.8	3.2	–4.1	3.2

only cover the years 2000–2004. Likewise, no EMEP emission estimates are available for V and only for individual years for Ni. The development of the V and Ni depositions at Valkea-Kotinen is a positive signal, which cannot be examined here in more detail because of inadequate emission estimates.

No statistically significant trends were found in Hg_{tot} deposition in any of the studied time series, although the mean values of the three time series decreased. Furthermore, during the first period of 1995–2004, an apparent decreasing trend was masked by two individual high monthly values. However, both of these peaks occurred in July, when the highest Hg_{tot} deposition is expected. When replacing these two values from the 10-year dataset of 120 values with July averages, a statistically significant annual trend of –3.1% ± 2.9% is found. Similarly, a decreasing trend during 1995–2002 was also found at five coastal stations around the North Sea in a study by Wängberg *et al*. (2007). The recorded decreases in deposition are mainly a result of improved control measures in coal power plants, which are the biggest anthropogenic-mercury emitters. While reducing SO_2 and particle emissions, desulphurization techniques also effectively lower Hg emissions.

Transport of air masses to Valkea-Kotinen

The site analysis of the IM stations demonstrated that possible changes at the Finnish IM stations are not due to changes in local emissions, and that Valkea-Kotinen was representative of clean areas in southern Finland (Ruoho-Airola *et al*. 1998). The main contributor to Finnish air quality and atmospheric deposition in background areas is long-range transport from different parts of Europe (Nyíri *et al*. 2010, Travnikov *et al*. 2012). Thus, estimation of the transport of air masses to Valkea-Kotinen indicates possible source areas of the atmospheric load. The transport pattern was compiled from the trajectories calculated in the EMEP programme for 1997–2006 (www.EMEP.int).

The sectoral distribution roughly illustrates the relative importance of different directions of transport to Valkea-Kotinen (Fig. 6). In summer (Fig. 6A), transport from the southwest, west, northwest and north dominated, while transport from the south, southeast and east was infrequent. In winter (Fig. 6B), the pattern of transport closely resembled the corresponding distribution in summer, and only a small shift from the sector towards the northeast to the sector towards the west was detected. The frequency of transport from different directions to Valkea-Kotinen in summer and winter did not change significantly during 1997–2006.

From the Finnish perspective, the emissions of sulphur dioxide are greatest in the countries to the south, southwest and west of Finland, whereas the strongest emission fields of NO_x and ammonia are located to the southwest and west of Finland (http://www.ceip.at/webdab-emission-database/). For many of the trace elements in this study, the most important source areas are located in the southeast to southwest sectors. Thus, changes in emissions in the sectors ranging from the southeast to the west contributed greatly to the air quality and atmospheric deposition at Valkea-Kotinen, as was shown to be the case for the S and N exposure in Ähtäri (Ruoho-Airola *et al*. 2004), located 160 km to the northwest of Valkea-Kotinen. The different development of NO_3^- deposition in Valkea-Kotinen as compared with that of the other elements might be connected to increased Russian emissions (Tørseth *et al*. 2012) and ship traffic emissions in the Baltic Sea (Bartnicki *et al*. 2010, 2011, Jalkanen *et al*. 2013), and the unchanged NO_x emissions in the EMEP domain (Fageli *et al*. 2012), all in the period 2002–2008.

Conclusions

A significant downward trend in bulk depositions of all main ions at Valkea-Kotinen was detected in the period 1988–1997. Moreover, for all trace elements except Cd and Hg_{tot}, bulk deposition declined during the first ten years of measurement. Depending on the component, the monitoring of trace elements began between 1990 and 1995, and for Al and Co in 2003. Significant downward trends were recorded during the entire measurement period for SO_4^{2-}, H^+, Pb, As, Ni and V, which provides positive evidence

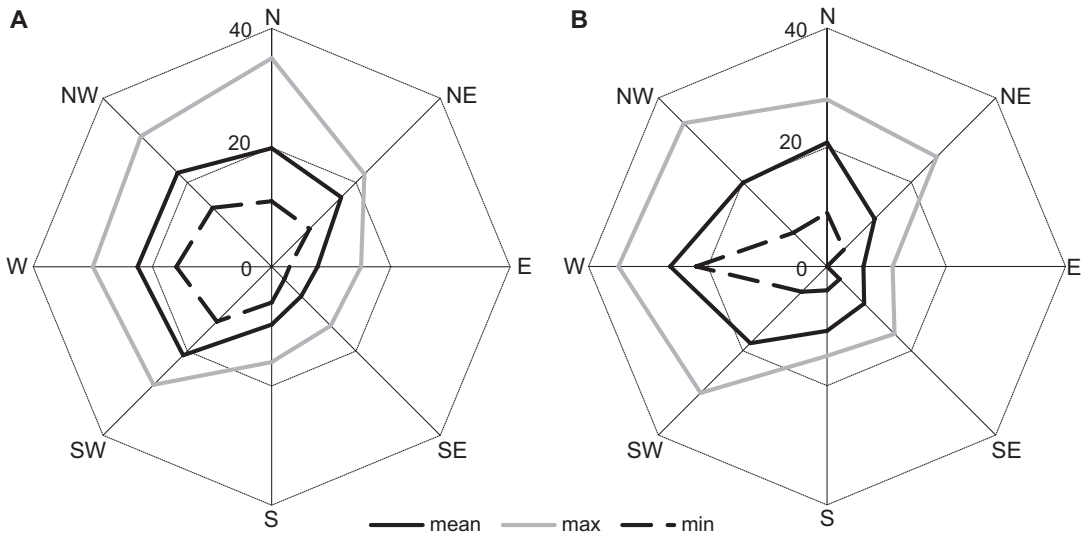

Fig. 6. Mean, maximum and minimum values for the transport of air from different sectors to the Valkea-Kotinen area in 1997–2006. Calculated as days of transport in the (**A**) summer and (**B**) winter seasons. Trajectory data from the EMEP programme (www.EMEP.int).

of successful emission reductions for these elements or their precursors.

In recent years, the N cycle in the environment has attracted increasing interest, one reason being the slower decline in N emissions as compared with that in S emissions. In contrast to the general decreasing trend for acidifying compounds, bulk deposition of NO_3^- increased during 2002–2008 at Valkea-Kotinen. Further studies might reveal whether the situation is similar at other background stations in Finland, and confirm our assumption that this negative development has resulted from increased Russian emissions, ship traffic emissions in the Baltic Sea and unchanged NO_x emissions in the EMEP domain in 2002–2008.

The high NO_3^- concentrations in groundwater are generally reported to result from agricultural activities. In the case of a large groundwater reservoir in a pristine state, the trend for atmospheric NO_3^- might strongly influence the water quality, as our results suggest. The hydrological continuum of NO_3^- in deposition to groundwater in Valkea-Kotinen should be studied in more detail, taking into account *inter alia* the soil and geological structure.

Bulk deposition of Cd increased by 2% annually between 1996 and 2005, after which no further significant changes were detected. An increase in Cd deposition was also detected at other Finnish background stations and in Russia in 2000–2005. Even though the levels measured at Valkea-Kotinen are low as compared with those in areas in central Europe, the element is highly enriched in the environment and harmful to ecosystems. The problem of no response in the Valkea-Kotinen catchment to the declining Cd emissions warrants deeper analysis.

The Integrated Monitoring programme has investigated the effects of atmospheric loading on ecosystems. Because the Valkea-Kotinen catchment is not substantially affected by local emissions but is rather under the effect of long-range pollutant transport, estimation of the transport pattern of air to the study area binds the results obtained in all of the articles in this special issue to the development of European emissions.

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